Biomass Processing Using Ionic Liquids for Jet Fuel Production

Wesley Henderson

North Carolina State University at Raleigh

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Final Report

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AFOSR Final Project Report

1. Cover Sheet

Principal Investigator:	**Dr. Wesley Henderson**
Institution:	North Carolina State University
Address:	Department of Chemical & Biomolecular Engineering 911 Partners Way Campus Box 7905 Raleigh, NC 27695-7905 phone: 919-513-2917 whender@ncsu.edu
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2. Objectives

This project addressed a critical need of the U.S. Air Force, namely the production of jet fuel from the renewable domestic resource lignocellulosic biomass. Biomass consists predominantly of three biopolymers—lignin, hemicellulose and cellulose. For fuel production, it is necessary to separate the cellulose from the other components and convert the cellulose to glucose. This can then be catalytically converted to liquid hydrocarbons. The lignin and cellulose, however, have very low solubility in conventional solvents making processing difficult. Typically a pretreatment step is used to break up the lignin and make the cellulose accessible to further hydrolysis to glucose. Pretreatment, however, is one of the most expensive steps in biomass processing. A new pretreatment method which efficiently separates the biopolymers is needed—one which is inexpensive and does not hinder subsequent processing steps. This research project explored the use of ionic liquids (ILs) (salts which are liquid at low temperatures (often below ambient) as solvents for the pretreatment of biomass materials. Such materials are highly soluble in a number of ILs. Little is currently known, however, about such mixtures.

This project's **Research Thrusts** included:
    Thrust 1: Preparation of a diverse range of ILs to identify the role of IL cations and anions in biomaterial dissolution,
    Thrust 2: Examination of biomaterial solubility and separation/recovery (by the addition of a nonsolvating solvent) by preparing both binary IL-solute solid-liquid and liquid-liquid and ternary IL-solute-solvent (solute = biomaterials and model compounds) phase diagrams, and
    Thrust 3: Examination of the activity of cellulase enzymes in ILs for the conversion of cellulose to glucose.
    Efforts to pursue Research Thrust 2 (preparation of phase diagrams between ILs and model compounds for biomass components) were unsuccessful as the mixtures do not crystallize readily. The exploration of IL-solvent mixtures for biomass dissolution was therefore pursued instead. This research thrust was also expanded to include the exploration of protic ionic liquids (PILs) as media for lignin extraction from biomass.

3. Status of Effort
Solvent Selection for Polysaccharide Regeneration from ILs or Solvent-IL Mixtures

Once cellulose or biomass is dissolved in an IL, it is regenerated as a solid by precipitation initiated through the addition of a nonsolvent. Nearly all relevant publications in the scientific literature report the use of water as the nonsolvent. The structure of the cellulose, however, is a key factor for its subsequent enzymatic digestibility. Therefore, a study was completed which examined the influence of the nonsolvent on the structure of the regenerated cellulose. The solvents used were deionized water (W), acetone (A), water-acetone (W/A - 50:50 vol%), ethanol (E), ethanol-acetone (E/A - 50:50 vol%) and isopropanol (IPA). Cellulose did not precipitate from the cellulose/IL mixtures (5 wt% cellulose) after the addition of pure acetone. Upon standing after mixing, the C/IL-A solution instead separated into two liquid phases. The dissolved cellulose was retained in the lower IL-rich phase. The acetone-IL mixtures can dissolve 5 wt% cellulose up to an 80 mol% acetone composition. Thus, the lack of precipitation is expected. In contrast, a precipitate immediately formed when water, ethanol, isopropanol, W/A or E/A was used as nonsolvents. For the water-containing nonsolvents (W or W/A), the amount of nonsolvent used to regenerate the dissolved cellulose was approximately twice the C/IL mixture volume. Regeneration from water resulted in large clusters/particles, whereas the organic solvents (ethanol or isopropanol) resulted in a spongy solid (**Fig. 1**). Acetone mixed with either water or ethanol was able to regenerate the dissolved cellulose—when mixed with water (W/A) or ethanol (E/A), particles or a spongy solid resulted, respectively.

The structural difference between the W- or W/A-regenerated cellulose samples and the ones obtained from organic solvents (E, IPA or E/A) were significant. Cellulose is polymorphic and can therefore adopt different crystalline structures. **Fig. 2** shows that untreated cellulose has the typical XRD powder pattern of crystalline cellulose-I. Cellulose regenerated from W or W/A was instead transformed into the cellulose-II crystal structure. Organic solvents (E, IPA and E/A), in contrast, resulted in amorphous cellulose. As demonstrated in **Fig. 3**, the dissolution and regeneration of the cellulose significantly increases the enzymatic digestibility of the cellulose. Further, cellulose regenerated with organic solvents (E, IPA or E/A) showed a significantly higher hydrolysis rate than the cellulose obtained from water (W or W/A) as the nonsolvent. In particular, the ethanol-regenerated cellulose had both a rapid hydrolysis rate, as well as a high glucose yield with close to complete conversion in 12 h. In summary, the results indicate that cellulose (dissolved in an IL) regenerated from water is crystalline with the cellulose-II structure. In contrast, regeneration from ethanol or isopropanol results in amorphous cellulose. This, along with the need for a much less
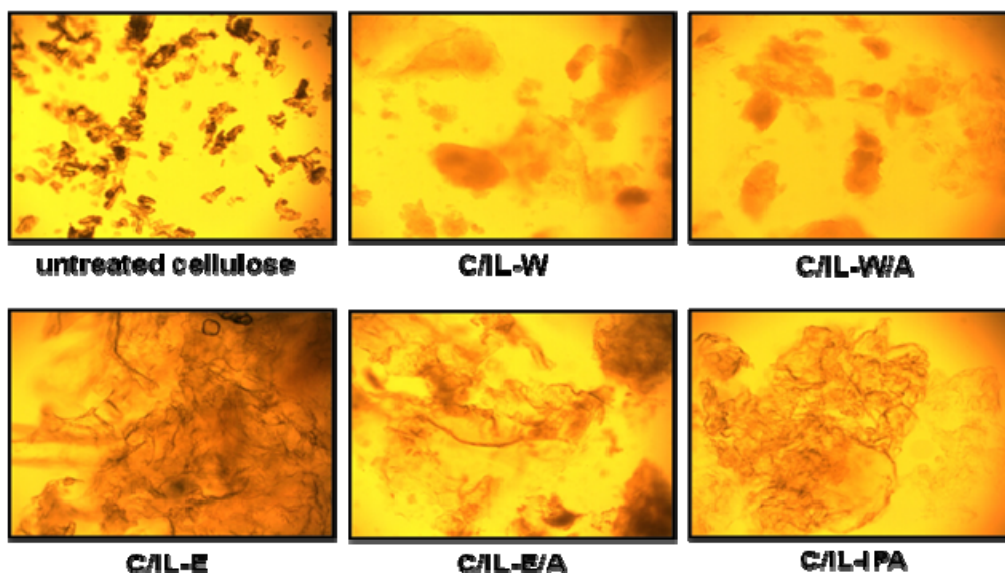

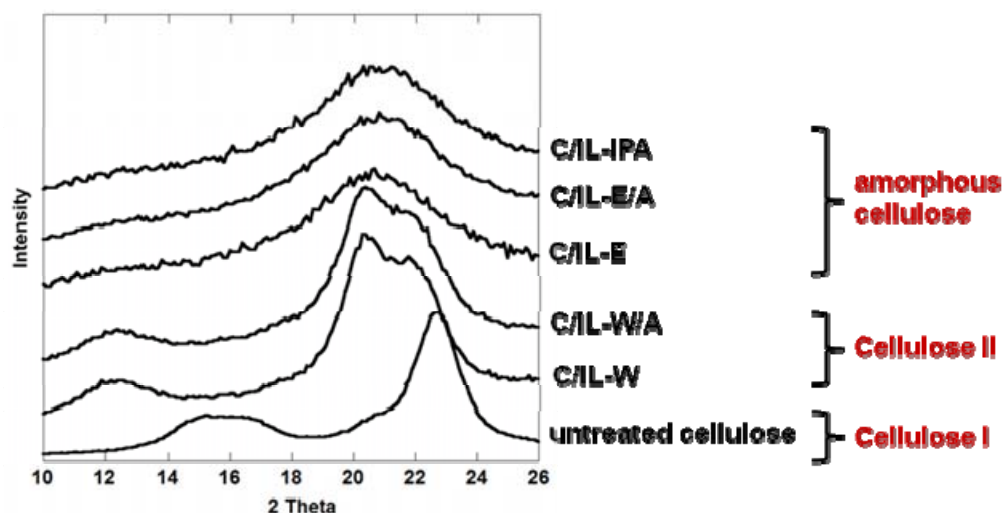**Fig. 1.** Microscope images (10x) of regenerated cellulose.

Fig. 2. Powder XRD data for the cellulose samples regenerated from different nonsolvents.

energy intensive distillation step to separate the solvent from the IL for recycling of the materials, suggests that ethanol is a preferable solvent to water for the regeneration step.

IL-Solvent Mixtures for Cellulose Dissolution

A method was developed during this project of using IL-solvent mixtures for cellulose/hemicellulose dissolution, instead of pure ILs. These mixtures are able to dissolve cellulose much more rapidly than the pure ILs alone while using only a fraction of the amount of IL (1/5 to 1/6 of what would typically be used). In addition, a method for easily recovering the IL-solvent mixtures has been demonstrated after the cellulose is regenerated using a nonsolvent.

Fig. 4 demonstrates that the choice of solvent for the IL-solvent mixtures is critical for determining the cellulose solubility with γ-butyrolactone (GBL) being much more effective than acetone. Many of the most favorable solvents for use in the IL-solvent mixtures have a

Fig. 3. Enzymatic hydrolysis of the cellulose samples regenerated from different nonsolvents.

high boiling point (e.g., GBL, DMSO, etc.). This initially suggested that the recovery of the IL and solvent might be problematic after the dissolution/regeneration of the cellulose, but this was found to not be the case. Once the cellulose is dissolved in the IL-solvent mixtures, it can be easily recovered by the addition of a nonsolvent (e.g., water or ethanol). This causes the cellulose to precipitate out of the solution as either crystalline cellulose (cellulose-II structure) or amorphous cellulose (**Fig. 5**). In particular, if ethanol is used as the nonsolvent, then the IL-solvent-nonsolvent solutions can be rotoevaporated at ambient temperature to selectively volatilize only the ethanol nonsolvent. The remaining IL-solvent solution then consists of the original IL-GBL mixture and this can be directly reused for cellulose dissolution. The resulting (cellulose II or amorphous) cellulose is highly amenable to enzymatic hydrolysis to glucose (**Fig. 5**).
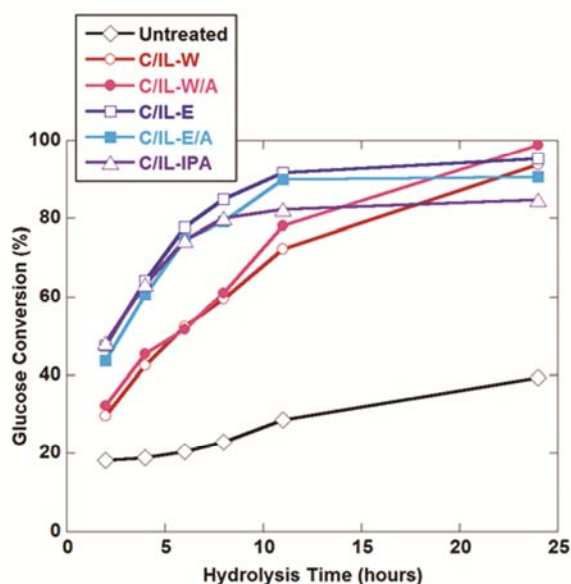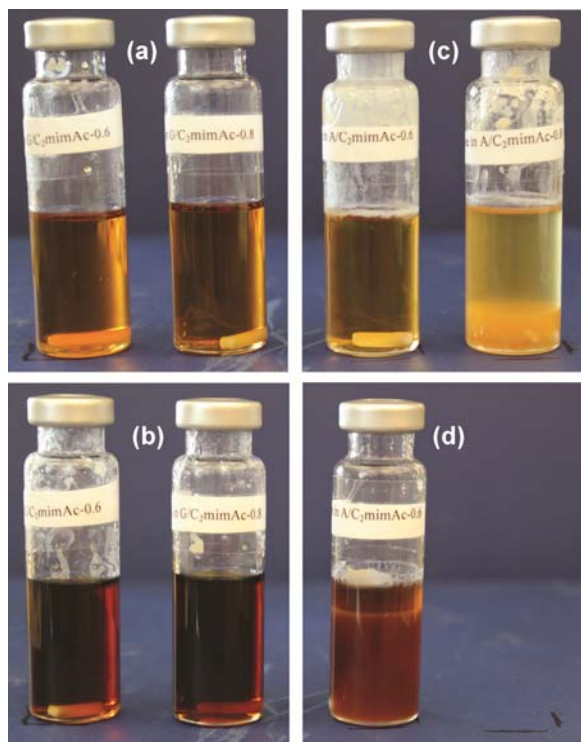
Fig. 4. Solvent-IL mixtures—(left) 60 mol% solvent and (right) 80 mol% solvent: (a) IL-GBL with 5 wt% cellulose, (b) IL-GBL with 10 wt% cellulose, (c) IL-acetone with 5 wt% cellulose and (d) IL-acetone with 10 wt% cellulose.

Fig. 5. (top) Powder XRD data for microcrystalline cellulose and cellulose samples regenerated from IL and solvent-IL mixtures (80 mol% GBL) mixtures with either water (W) or ethanol (E) as the nonsolvent and (bottom) enzymatic hydrolysis (cellulose conversion) of the samples.

PILs for Lignin Dissolution (Extraction)

During this project, it was discovered that protic ionic liquids (PILs)—salts formed from acid and base reagents, which typically melt below ambient temperature (**Scheme 1**)—can be used as an alternative to conventional (chemically intensive) lignin removal methods for biomass processing. In addition to the lignin removal, by taking advantage of the reversible exothermic reaction for PIL synthesis (**Scheme 1**) and the large difference in volatility between the PIL reagents and lignin, a procedure for the facile recovery/recycling of the PILs is available—i.e., once lignin has been extracted from biomass using a PIL, further separation via simple distillation is employed to recover the pure PIL leaving the extracted lignin available for further processing.

Three PILs with different cations (**Fig. 6**) were initially utilized to demonstrate the method and explore how the ion structure influences the lignin extraction. As PILs are formed via proton exchange, the extent of proton transfer (i.e., ion formation) has been linked to the difference in the pKa of the reagents (ΔpKa)—the greater the difference, the more the reaction is driven to the right (**Scheme 1**). Given that the pKa values for the reagents are Py 5.14, Mim 7.50, Pyrr 11.27, and HAc 4.76, this suggests that the ionicity should increase in the order:

[Py][Ac] < [Mim][Ac] << [Pyrr][Ac]
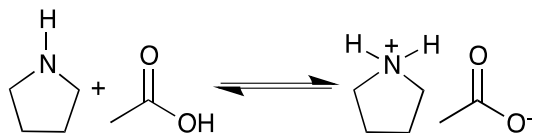
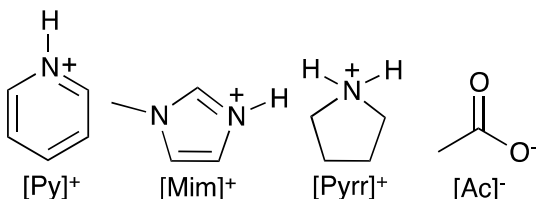**Scheme 1.** Formation of [Pyrr][Ac] from Pyrr and HAc.

[Py]⁺ [Mim]⁺ [Pyrr]⁺ [Ac]⁻

Fig. 6. PIL ions and their abbreviations: pyridinium [Py]$^+$, 1-methylimidazolium [Mim]$^+$, pyrrolidinium [Pyrr]$^+$ and acetate [Ac]$^-$.

Fig. 7. Variable-temperature TGA heating traces (5 °C min^{-1}) of reagents and PILs.

Table 1 Solubility of Kraft lignin, cellulose and xylan (% w/w) in the reagents and PILs (after heating/stirring at 90 °C for 24 h)

	lignin	cellulose	xylan
Py	> 50	0.10 ± 0.00	0.02 ± 0.02
Mim	> 50	0.24 ± 0.02	6.34 ± 0.17
Pyrr	> 50	0.63 ± 0.00	1.44 ± 0.07
HAc	0.7	0.07 ± 0.01	0.90 ± 0.04
[Py][Ac]	> 50	0.12 ± 0.03	0.82 ± 0.00
[Mim][Ac]	> 50	0.20 ± 0.05	5.60 ± 0.77
[Pyrr][Ac]	> 50	0.79 ± 0.04	> 15[a]

[a] Solubility limited by viscosity.

This conclusion is well supported by the thermal stability trends for the PILs (**Fig. 7**). Mass loss occurs at elevated temperature due to the formation and subsequent loss of volatile reagents. For the [Py][Ac] and [Mim][Ac] PILs, this occurs at temperatures only modestly higher that for the amines from which the salts are formed. For the [Pyrr][Ac] PIL, however, mass loss does not occur until a substantially higher temperature than for the highly volatile pyrrolidine (Pyrr) (**Fig. 7**) confirming that both proton transfer to the amine is largely complete and that the N-H bond formed is quite stable.

The solubility of biomass components in the PILs was determined initially using commercially available model biopolymers: lignin (Kraft lignin-Indulin AT), cellulose (microcrystalline cellulose) and hemicellulose (xylan from beech wood). The PILs, as well as the amine reagents used to synthesize them, are able to dissolve large amounts of Kraft lignin (**Table 1**). Furthermore, negligible solubility of cellulose in the reagents and PILs is noted. Xylan (the principal component of corn stover hemicellulose), on the other hand, has widely varying solubility in the different reagents and PILs. Notably, xylan is largely insoluble in Pyrr, HAc, and [Py][Ac]; is moderately soluble in Mim and [Mim][Ac]; and has a relatively high solubility in [Pyrr][Ac]. Given that [Pyrr][Ac] is more "ionic" than the other PILs, this suggests that the xylan solubility may originate from interactions with the salt ions. These results provide verification that PILs are able to dissolve large amounts of (Kraft) lignin, but little to no cellulose, which is necessary for the selective extraction (partitioning) of lignin for lignocellulosic biomass fractionation.

A second important consideration for a pretreatment step is the ease of the separation/ recyclability of the PIL after the lignin extraction. To demonstrate this, mixtures of the PILs with Kraft lignin were made and then separated using vacuum distillation (**Fig. 8**). The PILs were readily recovered and the leftover lignin maintained its thermal stability characteristics (implying that the lignin was largely unmodified) while exhibiting some changes in its physical appearance due to the precipitation from solution. Analogous recyclability experiments carried out with cellulose in the PILs confirmed that the recovered cellulose largely maintains its cellulose-I crystal structure due to the low solubility of cellulose in the PILs.
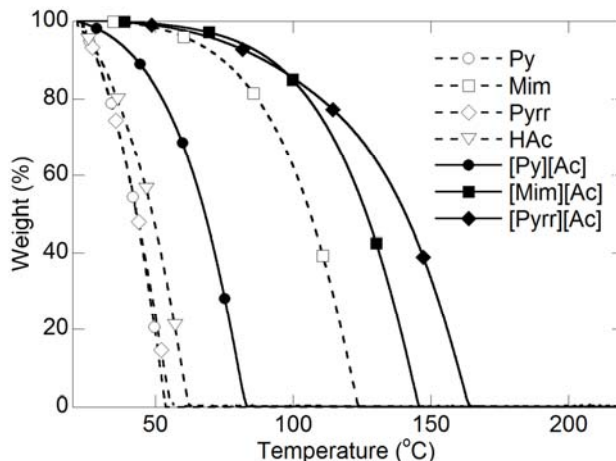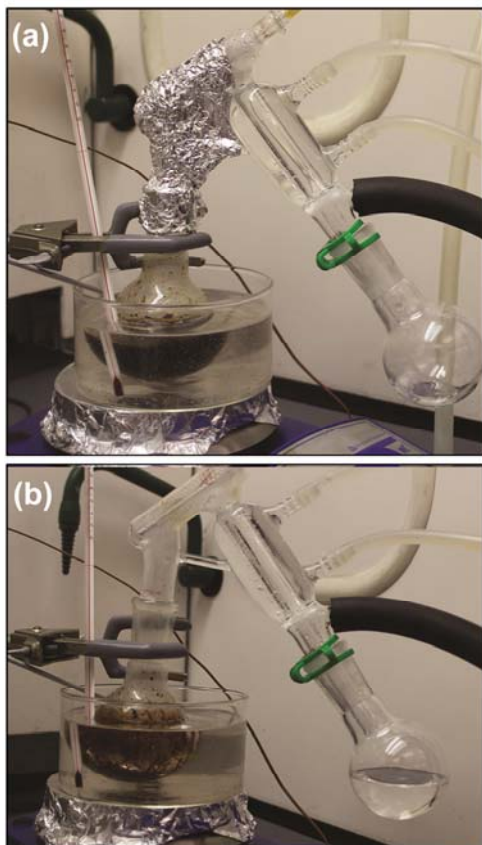
Fig. 8. Distillation set up used to separate PILs from lignin showing: (a) initial setup and (b) after complete collection of distillate.

Table 2. Composition (%) of PIL-CS after pretreatment (90 °C for 24 h)

	EF -CS	[Py][Ac] -CS	[Mim][Ac] -CS	[Pyrr][Ac] -CS
lignin	16.6	15.7	14.3	6.2
glucan	38.2	42.6	44.5	52.8
xylan	20.0	20.8	22.1	22.0
arabinan	2.5	1.3	1.8	2.9
galactan	1.1	0.9	0.8	0.8
mannan	0.1	0.0	0.2	0.2
ash	0.9	1.1	2.0	0.4
total sugars	61.9	65.6	69.4	78.7
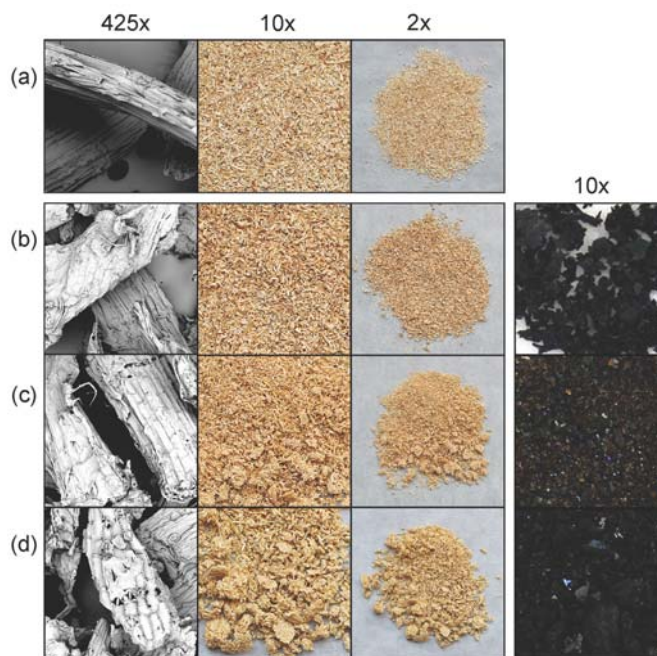
Fig. 9. Images depicting the CS fibers before and after PIL treatment and the recovered lignin from CS after PIL treatment: (a) EF-CS, (b) [Py][Ac]-CS, (c) [Mim][Ac]-CS and (d) [Pyrr][Ac]-CS.

The structure and properties of Kraft lignin, however, differ markedly from that of biomass lignin. The PILs were therefore then employed to pretreat extractive-free corn stover (EF-CS). After heating and stirring the EF-CS in the PILs (90°C for 24 h), the insoluble solids were separated by filtration from the liquid PIL filtrate. Compositional analysis of the solids (**Table 2**) revealed that the lignin extraction efficiency increased in the order:

[Py][Ac] < [Mim][Ac] << [Pyrr][Ac]

The PILs were then recovered from the mixture containing the extracted materials (lignin with a lesser amount of hemicellulose and other components) (Liquor 1) using vacuum distillation. The recovered PILs were characterized using ^{1}H-NMR analysis. The [Py][Ac] and [Mim][Ac] PILs were recovered as essentially pure PILs, but the [Pyrr][Ac] PIL contained a small amount of an amide impurity due to the extensive pretreatment time at elevated temperature.

The [Pyrr][Ac] PIL was able to extract greater than 70% of the lignin in the EF-CS, leaving a polysaccharide-rich stream (**Table 2**). Despite the high Kraft lignin solubility in all three PILs, the amount of CS-lignin extracted varied significantly for the three PILs (**Table 2**). The trend in lignin removal followed the trend in xylan solubility. SEM analysis of CS fibers before and after the PIL pretreatment confirmed that an increase in lignin removal corresponds with an increased disruption

Fig. 10. Corn stover (CS) lignin extraction procedure with PIL.

of the CS fibers (increase in the size of the fibers, as well as the formation of pores on the fiber surface - **Fig. 9**)—indicating that penetration of the CS fibers by the PILs has occurred as more lignin (and hemicellulose) is removed. Lignin found in the outer plant cell wall accounts for only about 20% of the lignin in biomass. In order to access the remainder of the lignin, one or more of the polysaccharides needs to be partially soluble in the PIL.

This work demonstrates that PILs are able to extract large amounts of lignin from biomass (**Fig. 10** and **Table 3**). The dissolution, to some extent, of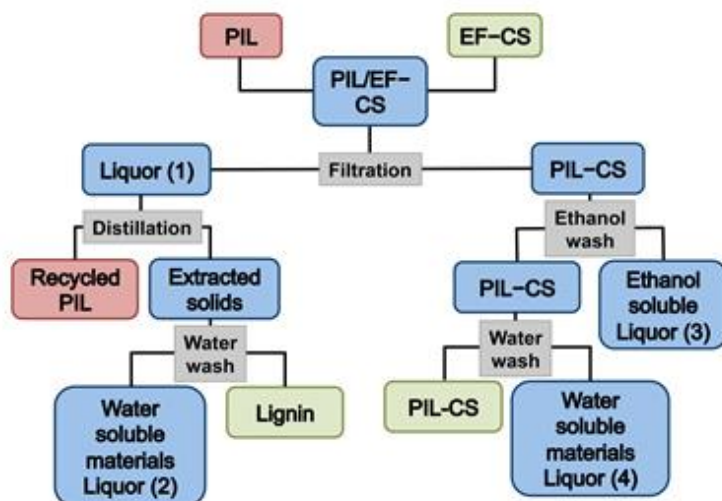 one or more of the polysaccharides, however, is necessary to enable PIL penetration of the fibers and full access to the lignin. Partial dissolution of xylan, the major hemicellulose component in CS, disrupts the fibers enough to attain a high lignin extraction efficiency. This preliminary work suggests that the solubility of xylan in the PILs may be directly proportional to the salt ionicity. Pure PILs can be recovered at yields approaching 100% using relatively mild heating conditions (with a partial vacuum). For full PIL recovery, however, a careful selection of the anions/cations used to synthesize the PIL is necessary to avoid PILs that are susceptible to the formation of amide by-products due to thermal degradation. The functionality/composition of the lignin extracted from the PILs appears to be largely retained relative to that for the native lignin. Further, after the PIL distillation step leaving the lignin-rich solids, the polysaccharides and sugars extracted by the PIL may be readily separated from the lignin by a simple water wash step. If this wash is then combined with the polysaccharide-rich solids, well over

Table 3 Composition of corn stover components after pretreatment with [Pyrr][Ac]—amount recovered, g (% w/w of initial component in EF-CS)

	lignin	glucan	xylan	arabinan	galactan	mannan	ash
EF-CS	0.833 (100)	1.913 (100)	1.000 (100)	0.126 (100)	0.053 (100)	0.005 (100)	0.040 (100)
extracted solids from [Pyrr][Ac] (Lignin)	0.606 (72.81)	0.067 (3.50)	0.009 (0.85)	0.006 (5.00)	0.001 (1.00)	0.000 (6.00)	0.029 (71.25)
water wash-lignin (Liquor 2)	0.025 (3.00)	0.204 (10.66)	0.311 (31.07)	0.028 (22.55)	0.026 (49.18)	0.004 (77.84)	-
[Pyrr][Ac]-CS (PIL-CS)	0.185 (22.19)	1.572 (82.17)	0.656 (65.53)	0.087 (68.95)	0.023 (43.32)	0.001 (12.52)	0.010 (25.00)
ethanol wash-CS (Liquor 3)	0.010 (1.20)	~ 0	~ 0	~ 0	~ 0	~ 0	-
water wash-CS (Liquor 4)	0.005 (0.60)	~ 0	~ 0	~ 0	~ 0	~ 0	-
total	0.831 (99.80)	1.834 (96.33)	0.975 (97.45)	0.122 (96.50)	0.050 (93.50)	0.005 (96.00)	0.039 (96.25)
Liquor 2 + PIL-CS	0.210 (25.19)	1.776 (92.83)	0.967 (96.60)	0.115 (91.50)	0.049 (92.50)	0.005 (90.36)	0.010 (25.00)

90% of the polysaccharides/sugars may be recovered with removal of approximately 75% of the lignin in the EF-CS (**Table 3**). Therefore, the use of PILs to selectively extract lignin from lignocellulosic biomass with high extraction efficiency and low waste generation is a quite promising means for the total utilization of lignocellulosic biomass—a necessary requirement for the implementation of a biofuel/biorefinery-based economy.

4. Accomplishments/New Findings

- Solvent-IL mixtures with only a fraction of the amount of IL typically used for biomass dissolution have been found to be equally effective (or superior) to the use of pure ILs at dissolving the polysaccharides in biomass substrates such as corn stover and switchgrass (but the presence of acidic protons is found to significantly inhibit cellulose solubility)—only about 1/6 as much IL is required (relative to the pure IL usage), much less IL is lost during the recovery/reuse steps (recycling), the cellulose dissolves much more rapidly in the IL-solvent mixtures than for the pure ILs and the viscosity of the IL-solvent mixtures can be readily tuned (unlike for pure ILs)
- Lignin may be selectively removed in high yield from the polysaccharides in lignocellulosic biomass using protic ionic liquids (PILs)—the PILs may then be readily separated from the extracted biomass components using distillation
- The regeneration solvent used (i.e., nonsolvent) has a significant impact on the resulting structure (and enzymatic hydrolysis efficiency) of the cellulose precipitated from IL-cellulose mixtures—ethanol may be a preferable solvent choice rather than water (which is currently widely used for this purpose)
- Although both chloride and acetate ILs (with 1,3-dialkylimidazolium cations) are able to dissolve cellulose well, the acetate ILs are also able to dissolve a significant amount of lignin (whereas the chloride ILs do not)—much of this lignin remains in the IL during the regeneration step in which the polysaccharides are precipitated from solution upon the addition of water
- Both the removal of lignin from biomass and the reduction in the cellulose crystallinity were demonstrated to be important factors for the efficient enzymatic hydrolysis of cellulose
- Given the importance of alkali-extraction for the pretreatment method demonstrated, the significance of the parameters for this step—namely liquid/solid (L/S) ratio, NaOH concentration, temperature of the wash and time stirred—have been analyzed…for overall glucose and xylose yield, the NaOH concentration is the most important factor—this is unfortunate because the cost of the NaOH is what limits the use of this pretreatment approach
- The Novozymes β-glucosidase enzyme that we have used has been found to be quite stable in alkali metal salts (chloride and acetate), but unstable in salts with organic cations (dialkylimidazolium and tetraethylammonium) such as the ILs—the reason for this is not yet known
- The combination of alkali extraction (of lignin) with IL dissolution of biomass has been demonstrated to be a highly effective pretreatment method for the conversion of raw cornstover into glucose—this enables the rapid conversion (hydrolysis) of the biomass, while minimizing the amount of enzyme necessary (also a crucial issue for a viable biomass conversion process due to the high cost of the enzymes)
- The balance of cation-anion and ion (cation and/or anion)-cellulose interactions is crucial for cellulose dissolution—if the ions are poor at forming hydrogen bonds, then cellulose dissolution is not possible—but, importantly, cellulose dissolution has also been demonstrated to not occur if the cation-anion interactions are too strong (even if the anions are capable of hydrogen bonding) as the ions preferentially interact with the neighboring counterions rather than with the cellulose
- Quite specific structural features of ions in an IL appear to be required for cellulose dissolution—a large number of ILs which are structurally related to ILs known to be effective cellulose solvents have been determined to be ineffective at dissolving cellulose

- The impurities present in commercial ILs, such as 1-butyl-3-methylimidazolium acetate, do not result in any significant variation in β-glucosidase cellulase enzyme activity—this is important since purification of ILs greatly increases their cost to manufacture
- The order in which the IL, enzyme and substrate are combined together is quite important—addition of the enzyme directly to the IL completely deactivates the enzyme—this is not the case, however, if the substrate is dissolved in the IL before the addition of the enzyme
- The cation of the IL has a major impact on the activity of the enzyme (as well as the ability of the IL to dissolve cellulose) despite the fact that the anion of the IL was expected to be the principal factor in enzyme stability since many of the IL cations are charge delocalized and/or poorly coordinating (the importance of the cation may stem from the role the cation plays in determining the anion's coordination)—the magnitude of this effect was unexpected

5. Personnel Supported
- **Wesley Henderson** (professor - PI)—one month of summer salary
- **Xinglian Geng** (laboratory manager)—100% of salary (full time) (for 4 years)
- **Ezinne Achinu** (graduate student - PhD)—100% of salary (full time) (for 3 years)
- **E. Kate Brown** (graduate student - PhD)—100% of salary (full time) (for 3 years)
- **Guoqing Ly** (graduate student - MS)—part-time salary (10 hr/wk)
- **Michael Brews** (undergraduate student)—no salary (course credit-undergraduate research)
- **Steven Mazur** (undergraduate student)—no salary (course credit-undergraduate research)
- **Reagan Howard** (undergraduate student)—no salary
- **Aaron Bailey** (undergraduate student)—part-time salary (10 hr/wk)
- **Oksana Bailey** (undergraduate student)—no salary (course credit-undergraduate research)
- **Jennifer Lewis** (undergraduate student)—part-time salary (10 hr/wk)
- **Emmanulla Sebeey** (undergraduate student) no salary (course credit-undergraduate research)
- **Brandon Jones** (undergraduate student)—no salary (course credit-undergraduate research)
- **William McDanel** (undergraduate student)—no salary (course credit-undergraduate research)

6. Publications
- Geng, X.; Henderson, W. A. Biotech. Bioengr. 2012, 109, 84-91. Pretreatment of Corn Stover by Combining Ionic Liquid Dissolution with Alkali Extraction.
- Achinivu, E. C.; Howard, R. M.; Li, G.; Gracz, H.; Henderson, W. A. Green Chem. 2014, 16, 1114-1119. Lignin Extraction from Biomass with Protic Ionic Liquids.

other manuscripts have been submitted for publication:
- Geng, X.; Brown, E. K.; Bailey, A.; Meng, J.; Henderson, W. A. Ionic Liquids and Biomass: Untangling Biomass Dissolution and Pretreatment Efficacy.
- Geng, X.; Henderson, W. A. submitted. Impact of Nonsolvents on the Structural Features and Enzyme Digestibility of Regenerated Cellulose from Ionic Liquid Dissolution.

manuscript drafts are also in-preparation or being revised from previous reviews:
- Brown, E. K.; Achinivu, E.; Henderson, W. A. in-preparation. Goldilocks—Too Soft-Too Hard: Influence of Ion Structure on Cellulose Solubility in Ionic Liquids.
- Brown, E. K.; Geng, X.; Ly, G.; Achinivu, E. C.; Henderson, W. A. in-preparation. Ionic Liquid-Solvent Mixtures: Tuning the Amount of Ionic Liquids Necessary for Cellulose Dissolution.
- Achinivu, E. C.; Marshall, G.; Williams, D.; Henderson, W. A. in-preparation. Ionicity and Hydrogen Bonding as Properties of Protic Ionic Liquids for Enhanced Lignin Extraction.
- Achinivu, E. C.; Marshall, G.; Brews, M.; Henderson, W. A. in-preparation. Lignin Extraction and Recovery Using Protic Ionic Liquids: Effects of Hydrogen Bonding.

7. Interactions/Transitions
a. Research results from this project were presented at:

- Pacific Northwest National Laboratory (PNNL)—Richland, WA, Sep 21, 2013—New Methodologies for Biomass Processing with Ionic Liquids (Invited Talk)
- Congress on Ionic Liquids (COIL-5)—Algarve, Portugal, Apr 21-25, 2013—New Methodologies for Biomass Processing with Ionic Liquids (Invited Talk)
- Spring 2013 MRS Meeting—San Francisco, CA, Apr 1-5, 2013—Biomass Separations with Ionic Liquids (Invited Talk)
- 245th ACS National Meeting—New Orleans, LA, Apr 9, 2013—Selective Removal and Recovery of Lignin Using Protic Ionic liquids (PILs) for a Cost-Effective Biomass Pretreatment Method
- Eastman Chemicals Workshop—NC State University—Aug 8, 2012 (Invited Talk)
- 2011 AIChE Annual Meeting, Minneapolis, MN, Oct 16-21, 2011—Lignocellulosic Biomass Dissolution in Ionic Liquid/Co-solvent Mixtures as a Pretreatment Method for Ethanol Production
- Novozymes North America, Inc., Franklinton, NC, July 21, 2011—Enabling Biomass Pretreatment with Ionic Liquids (Invited Talk)
- BIT's 1st Annual World Congress of Bioenergy. Innovations in Biorefineries Symposium. Dalian, China, Apr 25-29, 2011
- KIChE Meeting, Chang-Won, South Korea, Apr 28, 2011—Energizing Plug-In Hybrid Electric Vehicles: Enabling Advanced Batteries and Biofuels through the Use of Ionic Liquid-Solvent Mixtures (Invited Talk)
- Cellulose Short Course—NC State University, Department of Forestry Biomaterials, Raleigh, NC, Mar 7-10, 2011—Dissolution of Cellulose: An Exploration of Solvents and Salts (Invited Talk)
- 2011 Air Force Office of Scientific Research (AFOSR) Natural Materials, Systems & Extremophilles Program Review. National Harbor, MD, Jan 3-8, 2011—Biomass Processing Using Ionic Liquids
- Novozymes North America, Inc., Franklinton, NC, July 9, 2010—Enabling Biomass Pretreatment with Ionic Liquids (Invited Talk)
- Fall 2010 American Chemical Society National Meeting & Exposition, Boston, MA, Aug 22-26, 2010—Pretreatment of Cellulosic Biomass with Ionic Liquids for Biofuels Production (Invited Talk)
- AIChE Annual Meeting, Salt Lake City, UT, Nov 7-12, 2010—Ionic Liquids and Biomass: Untangling Biomass Dissolution and Pretreatment Efficacy
- 32nd Symposium on Biotechnology for Fuels and Chemicals, Clearwater Beach, FL, Apr 19-22, 2010—Influencing Factors in Alkali/Ionic Liquid Pretreatment for the Enzymatic Hydrolysis of Corn Stover
- 2009 Annual AIChE Meeting, Nashville, TN, November 8-13, 2009—Cellulose Dissolution in Ionic Liquids: Link Between Ion Structure and Cellulose Solubility
- ACS Southeastern Regional Meeting (SERMACS), San Juan, Puerto Rico, Oct 21-24, 2009—Cellulose Dissolution in Ionic Liquids: Link Between Ion Structure and Solubility
- 214th Electrochemical Society Meeting - Honolulu, HI - October 14, 2008—Exploring the Influence of Ionic Liquid Ion Structure on Cellulose Solvation

Henderson

b. Discussions occurred with Eastman Chemical Company on how to transition the work with IL-solvent mixtures (for cellulose dissolution) and perhaps the lignin extraction approach with PILs to their industrial processes. Eastman has recently formed a Center of Excellence at NC State University to form collaborations with faculty to resolve technical challenges for their chemical production and product lines. As a prime manufacturers of cellulose acetate and related products, they have shown significant interest in the IL-related work from the present project. Researchers at Kimberly Clark have also expressed considerable interest in the method developed to extract lignin using PILs.

We have also worked closely with Novozymes which has a research facility located just north of Raleigh, NC. Novozymes has provided the project with a variety of enzymes and the ILEET

laboratory participants have visited Novozymes several times to discuss the research results with a number of the senior Novozymes managers/researchers.

c.   Transitions. None

8. New Discoveries, Inventions, or Patent Disclosures

Invention Disclosure: (14-130) Lignin Extraction and Recovery from Biomass with Protic Ionic Liquids (PILs)

9. Honors/Awards

None